



**RAPID DISSOLUTION OF PLUTONIUM METAL
IN SULFAMIC ACID FOLLOWED BY
CONVERSION TO A NITRIC ACID MATRIX**

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Rapid Dissolution of Plutonium Metal in Sulfamic Acid
Followed by Conversion to a Nitric Acid Matrix

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Abstract

Plutonium metal dissolves readily in sulfamic acid; the dissolution rate is a function of surface area, sulfamic acid concentration, and temperature. Below a temperature of about 50°C the dissolution mechanism appears to proceed through a PuH_2 intermediate which yields a pyrophoric sludge. Above a temperature of about 60°C, neither the intermediate nor the sludge forms unless the sulfamic acid concentration drops below 0.4M. Overall dissolution rates of 400 to 500 g Pu/h per dissolver are obtainable with typical plutonium buttons.

Downstream processing requires conversion of the sulfamate to a nitrate medium. Approximately 90% of the residual sulfamate ion can be precipitated as sulfamic acid by the addition of two volumes of 72% HNO_3 to one volume of the plutonium sulfamate — sulfamic acid solution if the solution is chilled to -10°C. The small amount of sulfamate remaining can be oxidized either by diluting the nitric acid to about 3M and irradiating the solution with ultraviolet light or by diluting the solution with preirradiated 3M HNO_3 .

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Introduction

Plutonium metal that does not meet product purity specifications and aged plutonium metal into which ^{241}Am has grown must be recycled through a recovery and purification process. At the Savannah River Plant (SRP), the initial recycle step is dissolution of the metal. Sulfamic acid has been the accepted dissolvent in the SRP process since about 1962 (Gray, 1978).

Prior to 1962, mixtures of HNO_3 and HF were used to dissolve recycle plutonium metal (Jenkins, 1962 and 1963). The dissolution, however, is slow and the dissolvent is highly corrosive to stainless steel equipment. Fluoride and the aluminum added to decrease the corrosiveness of the fluoride become highly undesirable to downstream processing if ingrown ^{241}Am is to be recovered. To minimize processing problems downstream of dissolution, a dissolution method was needed that is rapid and that provides as near a pure plutonium nitrate — HNO_3 solution as possible.

Wheelwright and Fox (1977) developed an electrolytic dissolver for plutonium metal. Using a dissolver solution composition of 10M HNO_3 — 0.05M HF and a "traveling" cathode which maintained a minimum constant separation from the plutonium metal surface, the dissolver had a maximum dissolution rate of about 400 g Pu/h and an average rate of about 300 g Pu/h. This method, however, maintains the fluoride. Also, the high current density flowing through 10 to 14M HNO_3 results in NO_x gases which give visibility problems and off-gas handling problems.

Laboratory experiments at SRP have demonstrated that overall dissolution rates of 400 to 500 g Pu/h per dissolver can be obtained using 3.34M sulfamic acid at 70°C. Sludge formation, which is a major problem with room temperature sulfamic acid dissolution, is nonexistent if the sulfamic acid concentration is not allowed to drop below 0.4 to 0.5M. After the dissolution is complete, most of the residual sulfamic acid can be removed by precipitation, without carrying plutonium, by the addition of two volumes of 72% HNO_3 to one volume of dissolver solution. If the combined solutions are chilled to -10°C, approximately 85 to 90% of the sulfamate will precipitate as sulfamic acid. After dilution to about 3M HNO_3 , the residual sulfamate can be destroyed by irradiation with ultraviolet light or the solution can be diluted with preirradiated 3M HNO_3 .

Use of this flowsheet yields a solution which is acceptable to downstream processing even if ^{241}Am recovery is to be considered.

Experimental Procedure

Metal dissolution experiments were conducted in the apparatus shown in Figure 1. The volume of hydrogen gas generated as a function of time was determined for all plutonium dissolution rate experiments by measuring the volume of water displaced from the gas-tight reservoir. The volume of water displaced was measured using a graduated cylinder and it was corrected to standard temperature and barometric pressure. Plutonium metal turnings were used to determine the stoichiometry of the reaction. Reaction rates were determined on both alpha- and delta-phase plutonium metal. Reaction rates for alpha-phase metal were determined on pieces of plutonium removed from the SRP production dissolver. These pieces of metal were cut to size and their surface areas were calculated from dimensions measured with calipers. Reaction rates for delta-phase metal were determined on pieces of plutonium cut

from rolled sheets. The surface areas of these pieces of metal were also calculated from dimensions measured with calipers. The sulfamic acid solution was equilibrated to the temperature of a waterbath at the desired reaction temperature before the plutonium metal piece was introduced.

The solubility of sulfamic acid in various concentrations of HNO_3 was determined by allowing a known amount of sulfamic acid to come to equilibrium with a known volume of standardized HNO_3 solution at a measured temperature. After equilibrium was obtained, the crystals remaining were filtered, air-dried, and weighed.

Destruction of residual sulfamic acid in the solutions was demonstrated using a water-cooled ultraviolet lamp.

Stoichiometry

Table I shows the dissolution rates and total gas evolved for varying weights of plutonium metal turnings. These data show an average of $98.04 \pm 0.76\%$ of the theoretical $\text{H}_2(\text{g})$ was evolved, assuming the reaction is



A residue of from 0.1 to 1% of the original mass of sample remained after dissolution. X-ray diffraction analysis of the residues indicated the major component to be PuO_2 . Equation 1, therefore, is the correct stoichiometric relationship for the reaction.

Calculation of Button Surface Area

Plutonium buttons are produced in the ceramic liner (Figure 2) of a bomb reduction furnace. A typical button is 1.90 cm (0.75 in.) thick, weighs about 2250 g, and has a density of 19.3 g/cm^3 . To estimate the surface area, all surfaces were assumed to be smooth. For calculational purposes, the surface was divided into four segments: the first segment is a flat circle with a radius (r_1) of 4.763 cm; the second segment is the curved surface of the frustum of a right cone with a base radius (r_2) of

4.763 cm, a top radius (r_3) of 4.366 cm, and an altitude (h_1) of 1.1600 cm; the third segment is the curved surface of the frustum of a right cone with a base radius (r_2) of 4.3656 cm, a top radius (r_3) of 3.5719 cm, and an altitude (h_2) of 0.6250 cm; and the fourth segment is the curved surface of a spherical segment with a height (h_3) of 0.4800 cm, and the radius (r_4) of the sphere equal to 13.075 cm. The surface area of the button is then calculated with the equation

$$A = \pi \left[(r_1 + r_2) \sqrt{h_1^2 + (r_1 + r_2)^2} + (r_2 + r_3) \sqrt{h_2^2 + (r_2 - r_3)^2} + 2 r_4 h_3 + r_1^2 \right] \quad (2)$$

The volume of the button is calculated with the equation

$$V = (\pi/3) \left[h_3^2 (2r_4 - h_3) + h_2 (r_2^2 + r_2 r_3 + r_3^2) + h_1 (r_1^2 + r_1 r_2 + r_2^2) \right] \quad (3)$$

Both the surface area and the volume of a typical button are shown (Figure 3) as a function of mass of plutonium remaining undissolved. The surface of a typical button is calculated to be 171.2 cm² and the volume is calculated to be 116.4 cm³.

Dissolving Rates of Plutonium Metal

Hydrogen generation vs. time was determined for a series of plutonium metal pieces starting at varying temperatures. Typical uncorrected curves for these dissolutions are shown in Figure 4. The rate of dissolution was determined from the tangent of the early portion of the curve for evolved hydrogen gas. This value was divided by the initial surface area of the plutonium metal piece being dissolved to determine the rate of hydrogen evolved in terms of surface area [ml H₂/(min-cm²)].

Figure 5 shows the variation in the rate of hydrogen evolution from the dissolution of plutonium metal in 1.67M sulfamic acid as a function of temperature. With both alpha- and delta-phase metal there is a sharp break in the dissolution rate at about 50°C.

Figure 6 shows the variation in the rate of hydrogen evolution from alpha-phase plutonium at room temperature as a function of sulfamic acid concentration. Figure 7 shows the variation in the rate of hydrogen evolution from delta-phase plutonium at 70°C as a function of sulfamic acid concentration.

Although there is no explanation as to why alpha-phase plutonium metal dissolves faster than delta-phase metal, the data do suggest a possible explanation of the break in the dissolution rate curve at about 50°C. Since the formation of sludge appears to stop at the same temperature as the dissolution discontinuity, the sludge may be an intermediate which forms in the 20-50°C temperature dissolutions. The product which most closely fits the facts known about the sludge is a plutonium hydride, PuH_x . Below the temperature discontinuity, i.e., about 50°C, the dissolution apparently proceeds through the intermediate PuH_x ; above the temperature discontinuity, the intermediate apparently does not form. This intermediate would explain why the dry sludge is pyrophoric and shock sensitive. It would also explain the release of a gas and the retort when dry sludge suddenly ignites and why only PuO_2 is found in passivated sludge.

For calculational purposes, typical dissolving cycles were assumed to be:

- 1) charge a plutonium button to 3.0 L of sulfamic acid; 2) allow dissolution to proceed for a period of time; 3) displace 2.0 L of plutonium sulfamate - sulfamic acid solution with fresh sulfamic acid; 4) repeat steps 2 and 3 until the plutonium metal inventory decreases below a predetermined value; 5) charge another plutonium button; and 6) repeat steps 4 and 5 as long as necessary.

Using these assumptions, plutonium concentration, hydrogen off-gas rate, residual plutonium mass and surface area, and residual sulfamic acid concentration can be calculated as a function of time. Results for a variety of dissolving conditions are given in Table II.

Results obtained for room temperature dissolution of plutonium metal in 1.67M sulfamic acid agree very well with plutonium concentrations obtained from 3.0 L production-size dissolvers. In general, the first batches after startup of a cleaned-out dissolver will contain 45 to 55 g Pu/L. After the second button is charged to a dissolver heel of 1300 g Pu, plutonium concentrations will typically increase to 60 ± 10 g Pu/L. If the second button is charged to a dissolver heel of 1700 g Pu instead of 1300 g Pu, the plutonium concentration will typically increase to 70 ± 10 g Pu/L.

Increasing the temperature of 1.67M sulfamic acid dissolution is expected to increase the Pu concentrations to 100 to 125 g Pu/L. This one change decreases the sulfamate to Pu mole ratio from ~ 6.7 to ≤ 3.5 , eliminates sludge formation, and doubles the dissolution rate.

Increasing the sulfamic acid concentration of the dissolvent to 3.34M would retain a sulfamate to Pu mole ratio of < 3.5 , but it would redouble the dissolution rate over that of the 1.67M - 70°C dissolution. Or, compared to the 1.67M sulfamic acid - room temperature dissolution, the dissolution rate is increased by a factor of four.

Sludge Formation and Composition

On a laboratory scale (≤ 30 g Pu total), dissolution at ambient temperature (20-28°C) always left from 0.1 to 1% of the original mass of metal. On a production scale, the residue amounts, in general, to 0.1 to about 3% of the original mass. The residue was pyrophoric and shock sensitive but was easily passivated with dilute nitric acid. Additional sulfamic acid dissolved the residue if the solution was heated to 75°C. Attempts to identify the residue by x-ray diffraction indicated the major component to be PuO_2 . However, none of the samples which reached the x-ray

diffractometer were pyrophoric or shock sensitive; this indicates that the initial residue is oxidized to PuO_2 on contact with air. Dissolution of the metal at temperatures about 60°C , however, did not leave a residue unless the reaction was driven to a hydrogen ion concentration of less than about 0.4M. The rate controlling variable appears to change at about 1.7M sulfamic acid from diffusion of H^+ to the surface to diffusion of H_2 gas bubbles away from the surface.

Precipitation of Sulfamic Acid from Plutonium Sulfamate — Sulfamic Acid Solutions

When neither recovery of ingrown ^{241}Am nor storage of dissolved plutonium is to be considered, sulfamate ion poses no major problems for downstream processing other than extra waste costs. However, if either of these situations is to be considered, sulfamate ion poses major problems.

Sulfamic acid is moderately soluble in water (14.68 g dissolve in 100 g of water) at 0°C and 47.08 g at 80°C . All sulfamates, except the basic mercury salt, are very soluble. Lead, ammonium, sodium, and magnesium sulfamates are the most highly soluble; they are more soluble than the corresponding nitrates, sulfates, chlorides, and acetates.

The least soluble sulfamate salt, barium sulfamate (129 g or 0.088 mole per 100 g water at 25°C), cannot be used to precipitate the sulfamate because of the relative solubility of acceptable barium salts for barium addition to precipitate the sulfamate. The only common barium salts of sufficient solubility are chloride and acetate; neither of these are compatible with downstream processing in stainless steel equipment. Any attempt to remove the sulfamate ion from plutonium metal dissolving solutions then must depend upon its removal as sulfamic acid. Because the acid is moderately soluble, the volume of solution at the point of precipitation

must be minimized. Also, because the solubility of the acid is temperature dependent, the temperature should be reduced as much as practical to ensure maximum removal of sulfamate.

The solubility of sulfamic acid in HNO_3 is shown in Figure 8. When precipitated from either sulfamate - HNO_3 solutions or from Pu - sulfamate - HNO_3 solutions, sulfamic acid precipitates as orthorhombic crystals about 1 to 3 millimeters in size. When it was precipitated from Pu^{3+} solutions, the residual blue Pu^{3+} solution could easily be removed by washing with a small volume of cold, concentrated HNO_3 . The resulting washed crystals of sulfamic acid contained less than 1 μg of residual plutonium per gram of solid.

The solubility curve obtained was used to calculate the sulfamate remaining in solution at about 25°C as various amounts and concentrations of HNO_3 were added to the dissolver solution. The minimum solubility occurs when 2.0 to 2.25 L of concentrated HNO_3 is added per liter of dissolver solution. The solubility is about 20% less if 72% HNO_3 (15.7M) is used than if 64% (14.07M) HNO_3 is used.

Using 15.7M HNO_3 would reduce the sulfamic acid to 0.67 mole per liter of original dissolver solution. If 3.34 moles of sulfamic acid is used as the dissolvent, there is a reduction of 80% of the sulfamic acid fed to the dissolver. If 14.7M HNO_3 is used, the sulfamic acid would be reduced to only 0.84 mole per liter of original dissolver solution.

Additional sulfamate could be removed if the combined HNO_3 - dissolver solution were chilled below 25°C before the precipitated sulfamic acid was filtered. The amount of additional sulfamic acid removed would depend upon how low a temperature could be obtained within the available time in the processing cycle. Up to a maximum of about an additional 60% of residual sulfamic acid could be removed without freezing

the solution. Chilling, therefore, could reduce the amount of sulfamate ion in the final solution by 70 to 90% from the original solution.

Elimination of Residual Sulfamic Acid with UV Light

Any downstream processing of plutonium solutions requires that the plutonium be oxidized to the (IV) oxidation state. To accomplish this, sulfamate ion must be totally removed. This is accomplished by oxidizing the sulfamate to nitrogen gas and sulfate ion with nitrous acid. The classical method for generating nitrous acid is to add sodium nitrite. This, however, adds solids to the waste volume that must be processed and then stored. If ingrown ^{241}Am is to be recovered from the waste stream, sodium is even less desirable as it complicates americium recovery. Oxidation of the sulfamate with nitrous acid generated in situ with ultraviolet light, however, eliminates the problems generated by adding sodium ion to the system.

Results of attempts to oxidize sulfamate with UV light are shown in Figure 9. At approximately 10M HNO_3 , the reaction of nitrous acid with HNO_3 is more rapid than the reaction of nitrous acid with residual sulfamic acid. However, if the HNO_3 solution is diluted to about 3M, the reaction of nitrous acid with sulfamic acid is the faster reaction. Dilution of the solution to about 3M HNO_3 is therefore necessary before irradiation to allow the oxidation to proceed toward reasonable completion within convenient overall cycle times.

Since the HNO_3 must be diluted to allow the reaction to proceed, an additional option is available. Instead of irradiating plutonium containing solutions, a stock solution of nonradioactive 3M HNO_3 can be irradiated to generate the nitrous acid and this can then be used to dilute the 10M HNO_3 - Pu solution.

Conclusions

Processing of plutonium metal requires conversion to an aqueous solution that is compatible with both stainless steel process equipment and downstream processing of the solutions. This is best accomplished by dissolving plutonium metal in 3.34M sulfamic acid at 65 to 80°C. To make the solution more compatible with downstream processing, the sulfamic acid should be precipitated from the solution by adding chilled 72% HNO₃ to the dissolver solution, followed by further chilling of the resulting solution to about -10°C. For storage of the solution to await further processing, the Pu must be diluted from the approximately 80 g Pu/L - 10M HNO₃ to ≤6 g Pu/L and about 3M HNO₃. Downstream processing is further simplified if the 3M HNO₃ used for this dilution is first irradiated with UV light to saturate the HNO₃ with nitrous acid.

The solution presented for further processing contains only HNO₃, Pu(IV), and a small amount of sulfuric acid. If maximum use of the dissolution and removal system given were made, this procedure would dissolve about 8 kg Pu per 24-h day per dissolver (assuming 65% attainment) and present a solution for downstream processing containing little or no sodium and a sulfate to Pu mole ratio of <0.5. The sulfate to Pu mole ratio compares to 6.7 for the room temperature dissolution procedure which has been used for years.

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TABLE I
Dissolving Plutonium Metal Turnings

Pu, g	Plutonium Dissolution Rate, g/h per g Pu charged	Hydrogen Evolution Rate, ml/sec per g Pu charged	Volume of Hydrogen Evolved, ml		
			Measured		Theoretical (STP)
			Uncorr	At STP	
5.6600	37.14	1.047	840	773	796
3.6846	30.20	0.8530	550	507	518
6.0020	30.43	0.8628	910	836	845
4.0021	-	-	600	552	562

TABLE II
Plutonium Button Dissolving Under Various Conditions

Sulfamic Acid, molar		→ 1.67		1.67		3.34	
Temperature, °C →		25		70		70	
<u>Time, min</u>	<u>Pu, g/l</u>	<u>NH₂SO₃⁻/Pu mole ratio</u>	<u>Pu, g/l</u>	<u>NH₂SO₃⁻/Pu mole ratio</u>	<u>Pu, g/l</u>	<u>NH₃SO₃⁻/Pu mole ratio</u>	
1st Cut							
0	0		0		0		
15	19	21.0	44	9.1	54	14.8	
30	33	12.1	73	5.5	106	7.5	
45	42	9.5	92	4.3	153	5.2	
60	50	8.0	105	3.8	188	4.2	
75	57	7.0	114	3.5	211	3.8	
2nd. Cut							
0	13	30.7	37	10.8	75	10.6	
15	28	14.3	66	6.1	110	7.3	
30	42	9.5	85	4.7	161	5.0	
45	48	8.3	100	4.0	190	4.2	
60	55	7.3	110	3.6	210	3.8	
75	60	6.7	118	3.4	225	3.5	

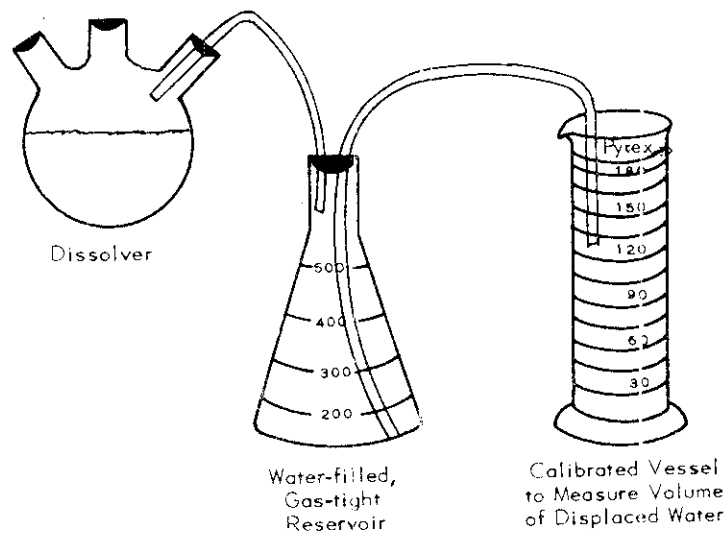


FIGURE 1. EXPERIMENTAL APPARATUS

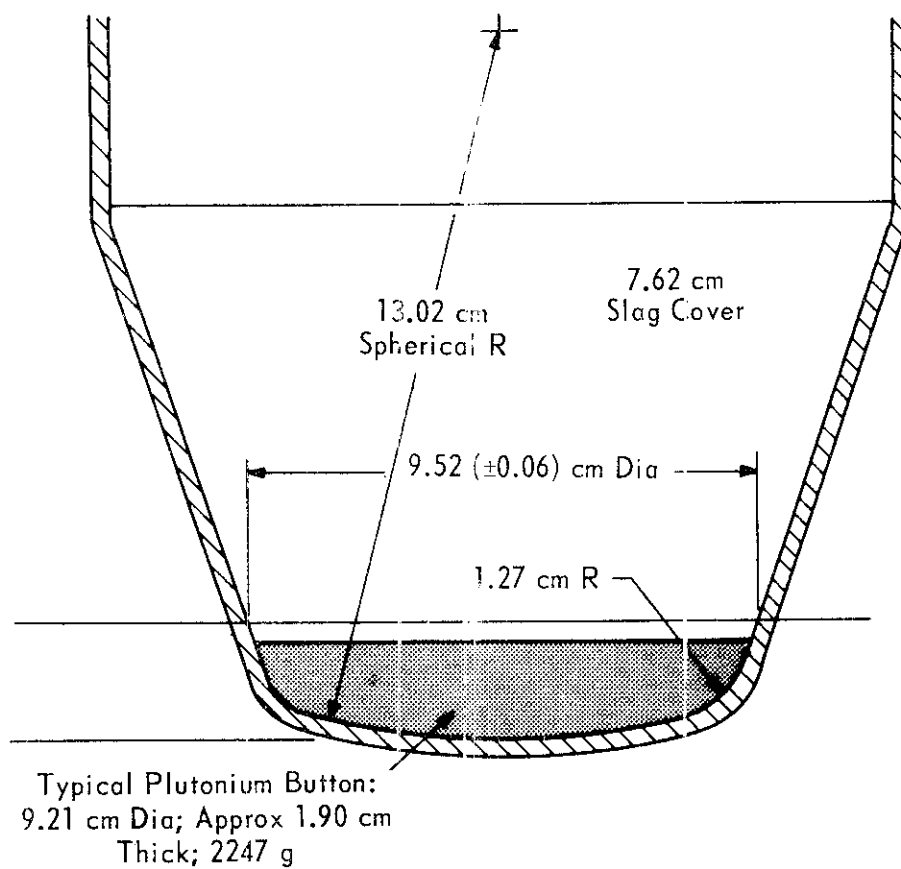


FIGURE 2. CERAMIC CRUCIBLE FOR PREPARING PLUTONIUM BUTTONS

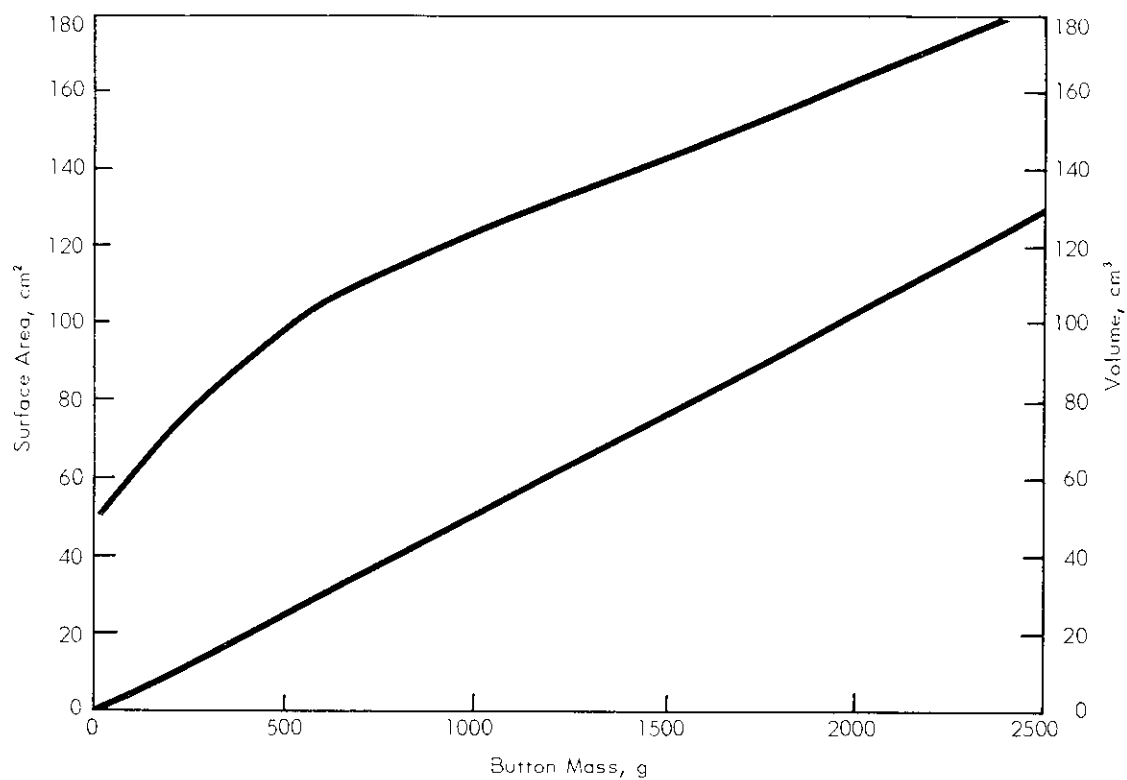


FIGURE 3. CALCULATED SURFACE AREA AND VOLUME OF A TYPICAL PLUTONIUM BUTTON DURING DISSOLUTION

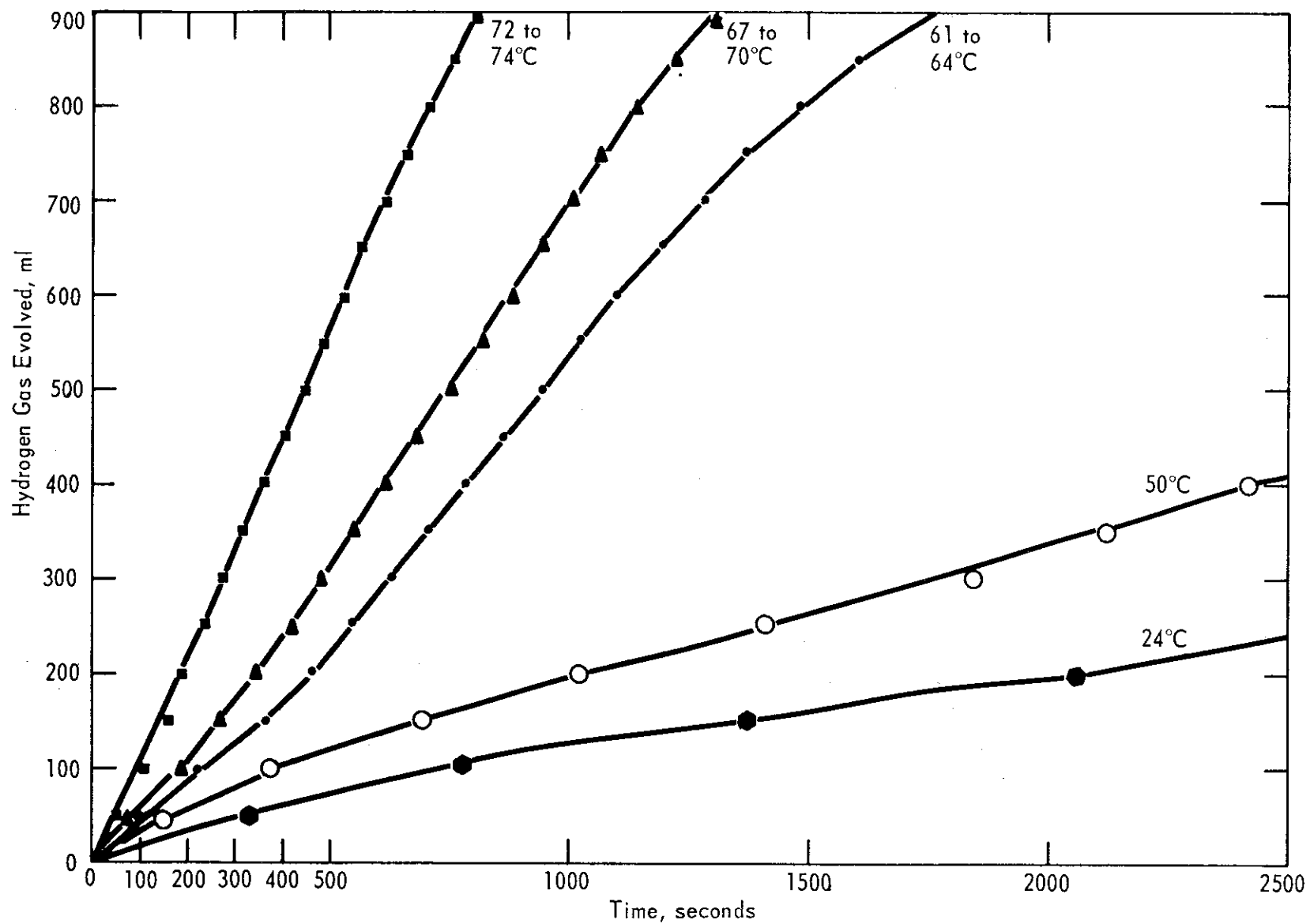


FIGURE 4. TYPICAL UNCORRECTED HYDROGEN GENERATION CURVES

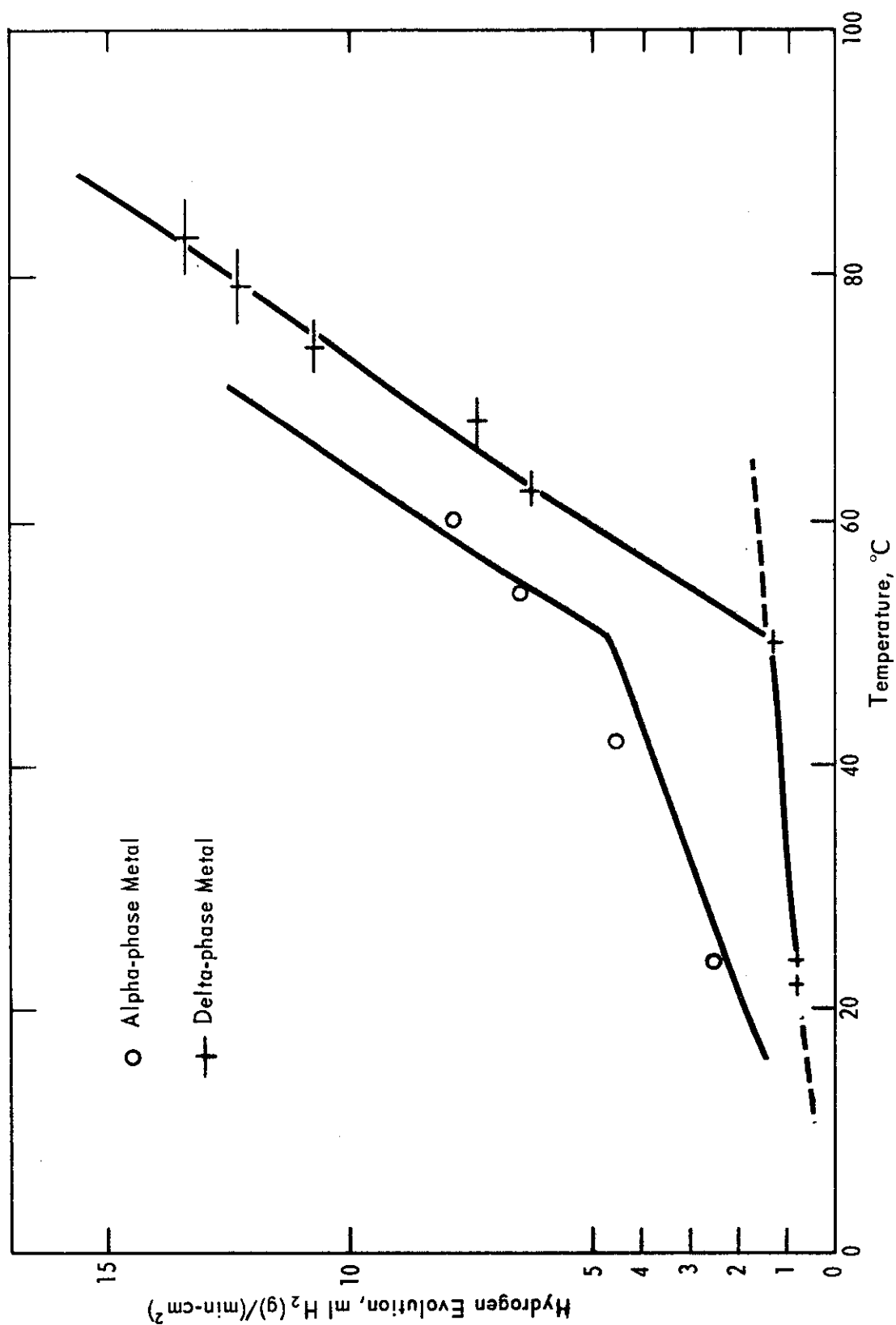


FIGURE 5. RATE OF HYDROGEN EVOLUTION FROM DISSOLUTION OF PLUTONIUM METAL IN 1.67M SULFAMIC ACID

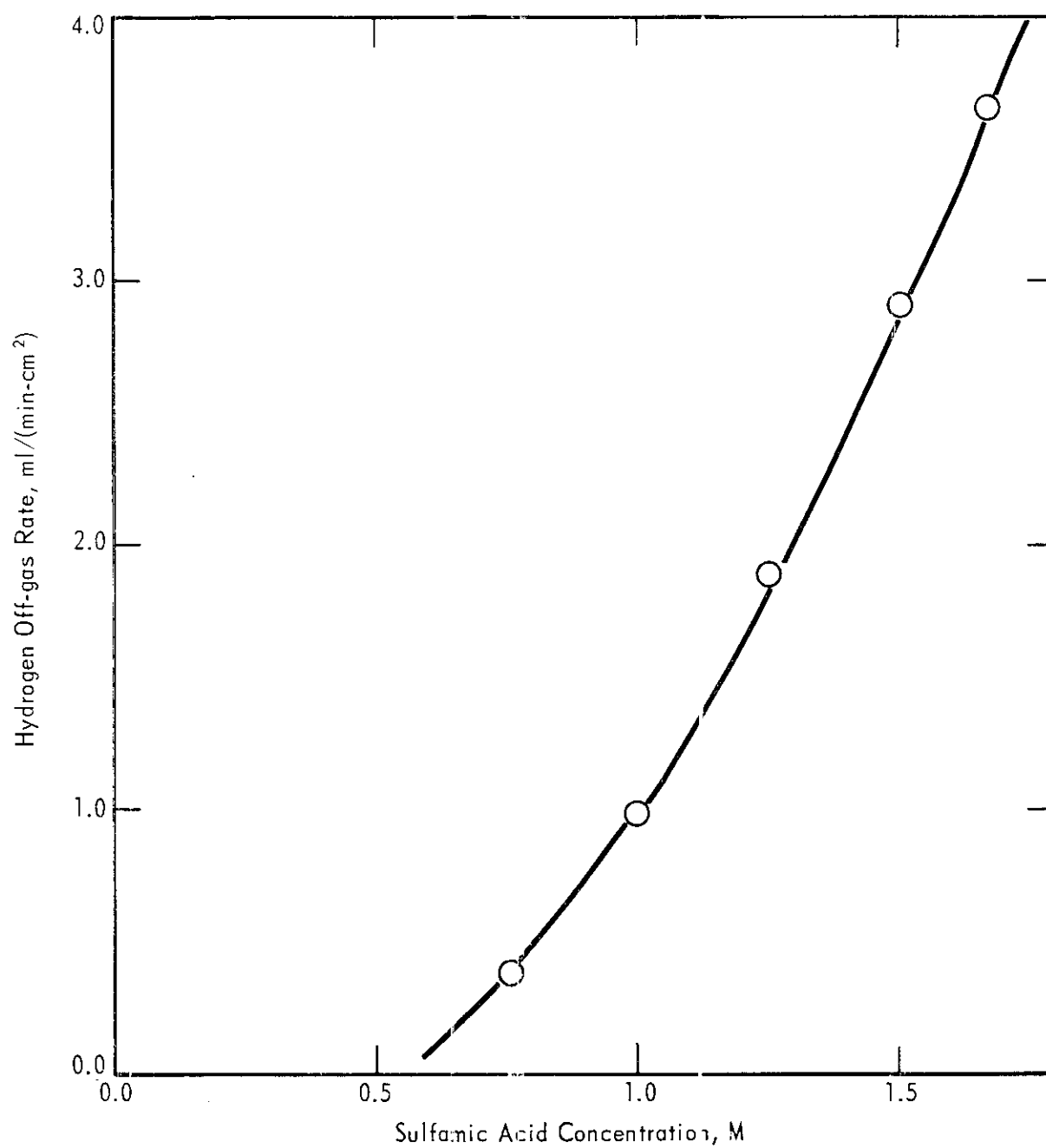


FIGURE 6. RATE OF DISSOLUTION OF PLUTONIUM METAL AS A FUNCTION OF SULFAMIC ACID CONCENTRATION (ROOM TEMPERATURE)

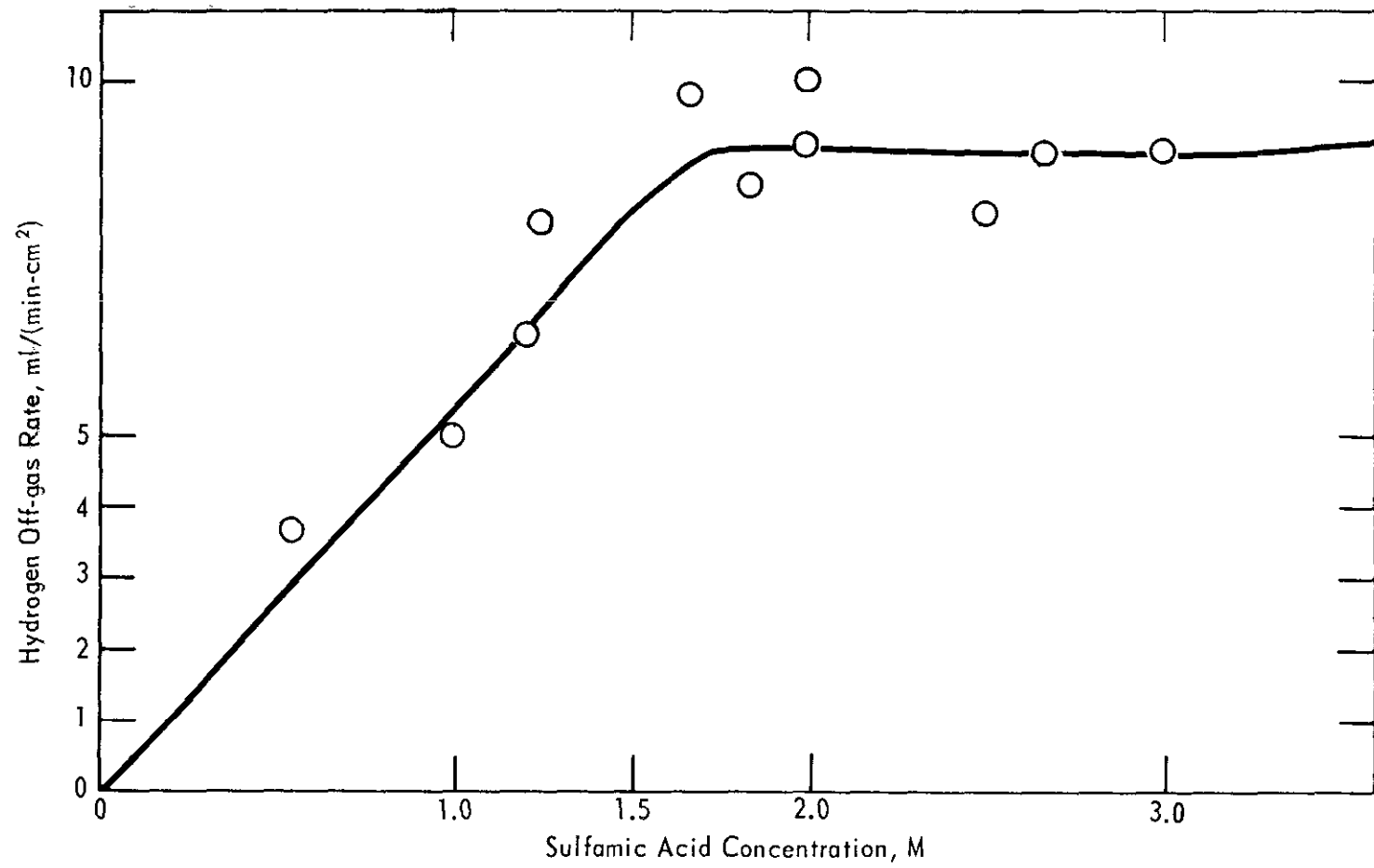


FIGURE 7. UNCORRECTED RATE OF DISSOLUTION OF PLUTONIUM METAL AS A FUNCTION OF SULFAMIC ACID CONCENTRATION (TEMPERATURE 70°C)

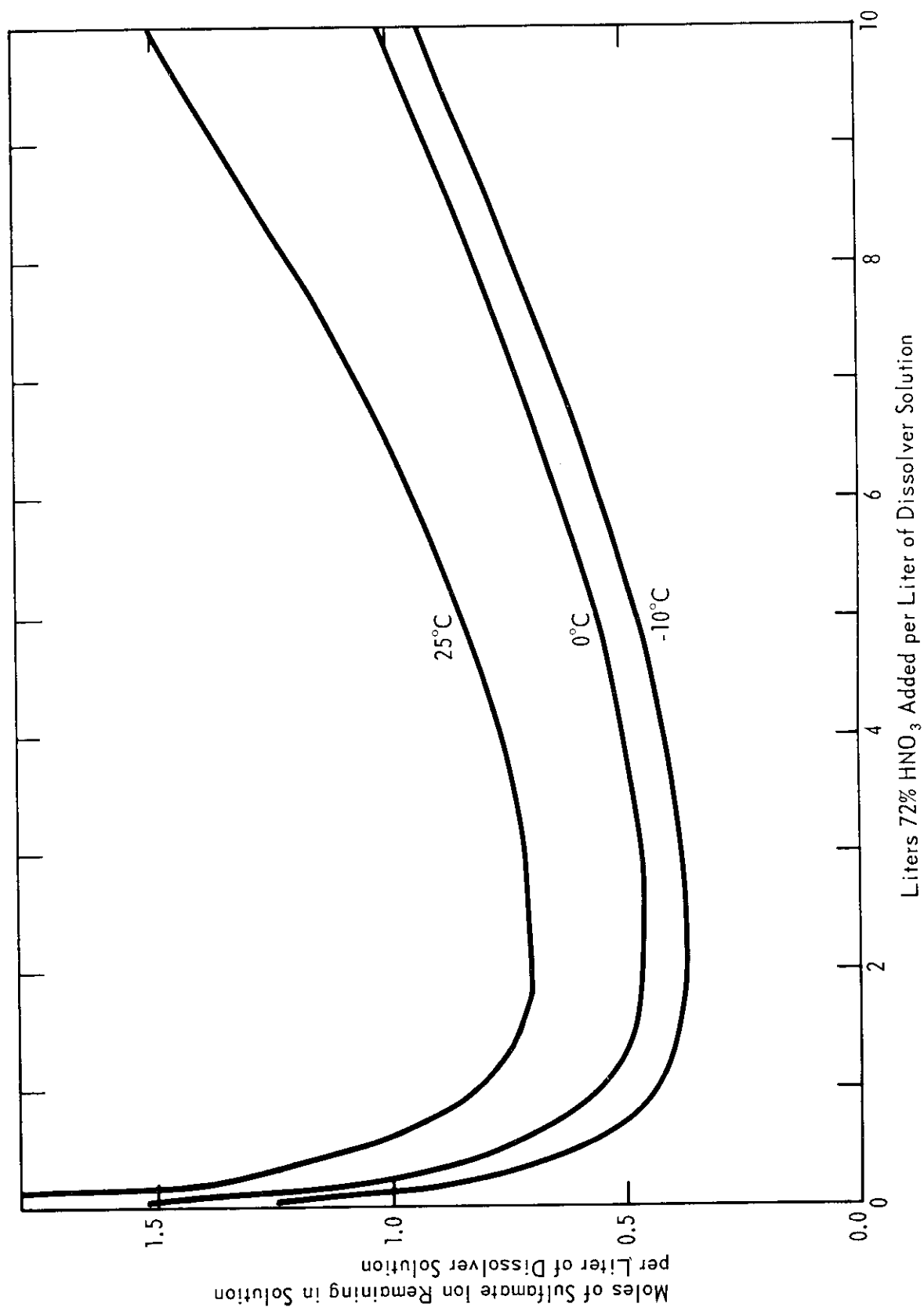


FIGURE 8. RESIDUAL SOLUBILITY OF SULFAMIC ACID IN NITRIC ACID

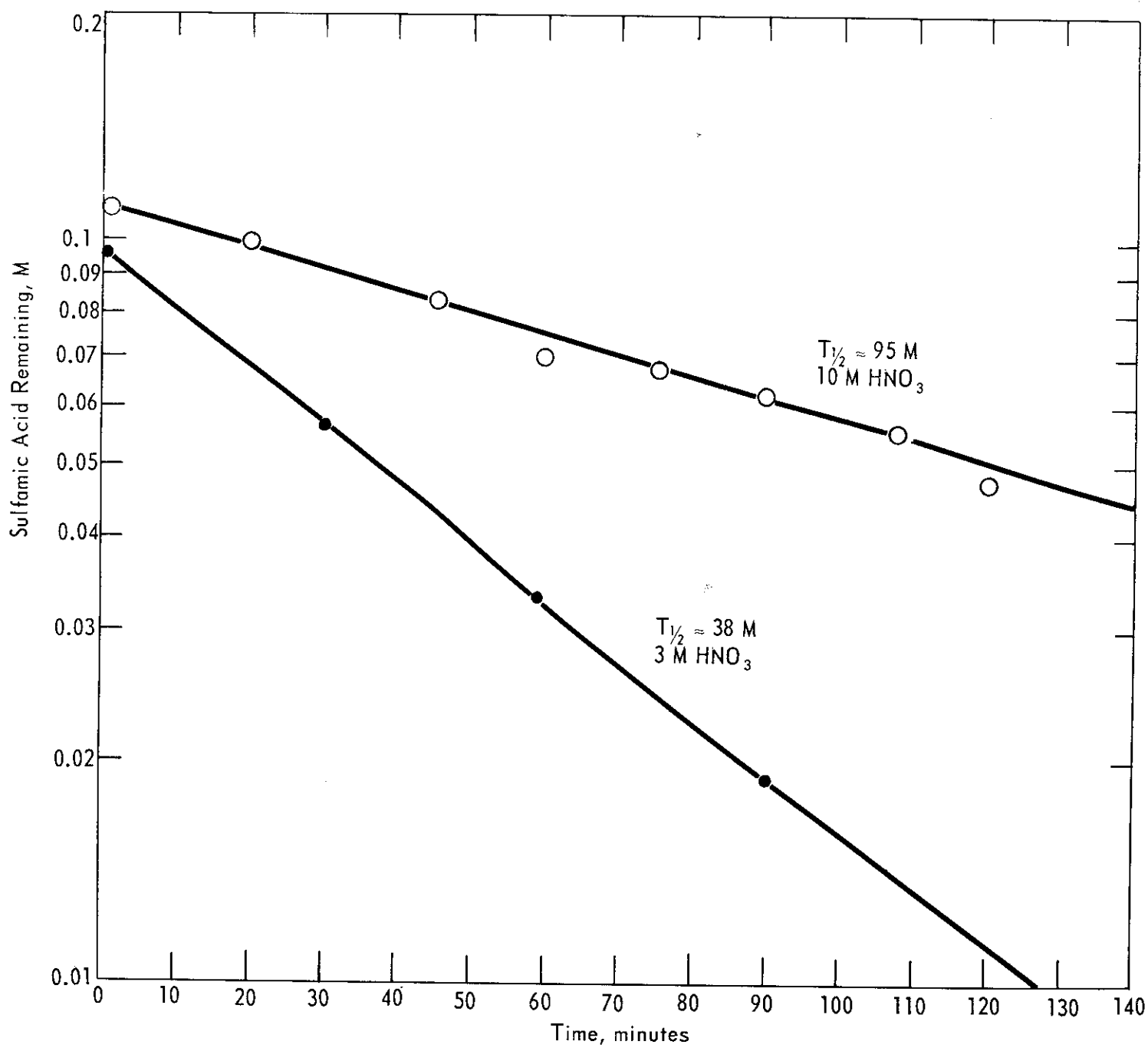


FIGURE 9. OXIDATION OF SULFAMIC ACID WITH NITRIC ACID AND ULTRAVIOLET LIGHT



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